Graduate Quantum Mechanics II - Problem Set 3 - Solution

Problem 1)

In the previous HW Problem, we have already shown that the spatial part of the eigenfunctions of the Hamiltonian can be chosen as eigenfunctions to $P$ (the total momentum) with eigenvalue $P \neq 0$, and to the “number operator” for the harmonic oscillator with eigenvalue $n$:

$$\psi_{P,n}(x_1,x_2) = \frac{1}{\sqrt{2\pi \hbar}} e^{iP(x_1+x_2)/\hbar} \left( \frac{\mu \omega}{\pi \hbar} \right)^{1/4} \sqrt{\frac{1}{2^n n!}} H_n \left( \frac{\mu \omega}{\hbar} (x_1-x_2) \right) e^{-\mu \omega (x_1-x_2)^2/2\hbar}$$

where $E = E_1 + E_2 = \frac{P^2}{2M} + \left(n + \frac{1}{2}\right) \hbar \omega$. (Note: Here $m_1 = m_2 = m$, so $M = 2m$ and $\mu = m/2$).

This has to be combined with the spin wave functions of two spin-1/2 particles, of which there are four possibilities:

$$|\chi_1\rangle = |S = 1, M = 1\rangle = |\uparrow \uparrow\rangle; \quad |\chi_2\rangle = |S = 1, M = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle);$$

$$|\chi_3\rangle = |S = 1, M = -1\rangle = |\downarrow \downarrow\rangle; \quad |\chi_4\rangle = |S = 0, M = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle)$$

a) Therefore, all solutions to the Schrödinger Equation (ignoring antisymmetrization) have the form $|\psi_{P,n}\rangle \otimes |\chi_i\rangle$, $i = 1\ldots 4$.

b) Under exchange of particle 1 with particle 2 (i.e., $x_1$ with $x_2$), the parts $e^{iP(x_1+x_2)/\hbar}$ and $e^{-\mu \omega (x_1-x_2)^2/2\hbar}$ of the spatial wave function are obviously symmetric (unchanged). The only part that is “non-trivial” is $H_n \left( \frac{\mu \omega}{\hbar} (x_1-x_2) \right)$ which is even (unchanged) for even $n = 0, 2, 4, \ldots$ (in which case $H_n$ is a polynomial with even powers of $(x_1 - x_2)$ only) and odd (acquiring an overall minus sign) if $n = 1, 3, \ldots$ is odd. Vice versa, $\chi_1 - \chi_3$ are even under particle exchange and $\chi_4$ is odd. This means that only the combinations under a) for which either $n$ is even, $i = 4$ or $n$ is odd, $i = 1, 2, 3$ are properly antisymmetrized for a 2-fermion wave function.

c) To find the normalization, we have to do the following integral:
\[ \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \langle \chi_i | \otimes \psi_{P,n}^* (x_1,x_2) \cdot \psi_{P,n} (x_1,x_2) \otimes | \chi_i \rangle = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \psi_{P,n}^* (x_1,x_2) \cdot \psi_{P,n} (x_1,x_2) \]

\[ = \frac{1}{2\pi \hbar} \left( \frac{\mu \omega}{\pi \hbar} \right)^{1/2} \frac{1}{2^n n!} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx_2 H_n^2 \left( \frac{\mu \omega}{\hbar} (x_1 - x_2) \right) e^{-\mu \omega (x_1 - x_2)^2/\hbar} = \text{Int} \]

(since the spin wave functions are already properly normalized to 1). This integral can be done directly (first keep \( x_1 \) fixed and replace the integral over \( x_2 \) with one over \( y = x_1 - x_2 \)). Alternatively, since \( x_1 = X + \frac{1}{2} x \) and \( x_2 = X - \frac{1}{2} x \), it follows that

\[
\begin{vmatrix}
\frac{\partial x_1}{\partial X} & \frac{\partial x_1}{\partial x} \\
\frac{\partial x_2}{\partial X} & \frac{\partial x_2}{\partial x}
\end{vmatrix} = \begin{vmatrix} 1 & \frac{1}{2} \\ 1 & -\frac{1}{2} \end{vmatrix} = \left| -\frac{1}{2} - \frac{1}{2} \right| = 1 \Rightarrow dx_1 dx_2 = dX dx \Rightarrow
\]

\[ \text{Int} = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dX \frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{\infty} dy H_n^2 (y) e^{-y^2} \quad \text{with} \quad y = \frac{\mu \omega}{\hbar} x. \]

The expression after “dX” is completely equivalent with the normalization condition for the usual 1-dimensional harmonic oscillator eigenfunctions, i.e. it is already equal to 1.

The remainder gives \( \text{Int} = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dX \) which is of course un-normalizable, but is exactly what you would get for any simple 1-dimensional “free eigenstate” of fixed momentum.

So we can consider it properly normalized, as well. The end result of this “exercise in futility” is simply to show that the wave function was already properly normalized, without the need to introduce any more normalization factors.

From part b) and the previous HW problem set, we know already that all energy eigenvalues \( E > \frac{\hbar \omega}{2} \) are allowed, since for each quantum number \( n \) there is at least one solution that is properly antisymmetrized. In fact, each such eigenvalue is at least twice degenerate (for \( \pm P \)), also as already shown. For the range \( \frac{\hbar \omega}{2} < E < \frac{3}{2} \hbar \omega \), there are only these two possibilities, since we ascertained that \( S = 0 \) (\( n = 0 \) means the spatial part is symmetric so the spin part must be antisymmetric). However, for \( \frac{3}{2} \hbar \omega < E < \frac{5}{2} \hbar \omega \) there are now several more options: The same two as before (just with larger \( P \)) plus the 6 more for the \( n=1, S=1 \) wave function (which has 3 possible values for \( M \) times 2 for \( P \)). As \( E \) increases, we keep adding alternatively 2 and then again 6 more possible states, so that the degeneracy increases in small and large steps.

d) After a measurement that finds one of two identical fermions, one at \( x_1 \) and the other at \( x_2 \), the system must be in an antisymmetrized basis state
\[ |\psi_{\text{final}}\rangle = \frac{1}{\sqrt{2}} (|x_1\rangle |x_2\rangle + |x_2\rangle |x_1\rangle) \otimes |0,0\rangle \] or
\[ |\psi_{\text{final}}\rangle = \frac{1}{\sqrt{2}} (|x_1\rangle |x_2\rangle - |x_2\rangle |x_1\rangle) \otimes |1,M\rangle \]
where \( S \) and \( M \) are the same as in the initial state. For given \( P \), the lowest energy eigenfunction has \( n=0 \) if \( S=0 \), and we have the overlap
\[
\frac{1}{\sqrt{2}} \langle 0,0 | \otimes \left( \langle x_1 | \langle x_2 | + \langle x_2 | \langle x_1 | \right) |\psi_{\text{f,0}}\rangle \otimes |0,0\rangle =
\]
\[
\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} \frac{1}{2^{\frac{1}{4}}} \left[ e^{iP(\langle x_1 \rangle \langle x_2 \rangle) / \hbar} H_0 \left( \frac{\mu \omega}{\hbar} (x_1 - x_2) \right) e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar}
+ e^{iP(\langle x_2 \rangle \langle x_1 \rangle) / \hbar} H_0 \left( \frac{\mu \omega}{\hbar} (x_2 - x_1) \right) e^{-\mu \omega (x_2 - x_1)^2 / 2\hbar} \right]
= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} \frac{1}{2^{\frac{1}{4}}} e^{iP(\langle x_1 \rangle \langle x_2 \rangle) / \hbar} e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar}
\]
\((H_0(y)=1)\). For the probability density, we need to take the absolute square of this result:
\[
dP(x_1,x_2) = \frac{1}{\pi \hbar} \sqrt{\frac{\mu \omega}{\pi \hbar}} e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar} \, dx_1 \, dx_2 \]
Note that this probability looks like a Gaussian with a maximum at zero distance between the two particles!
e) In complete analogy, we get for the overlap
\[
\frac{1}{\sqrt{2}} \langle 1,0 | \otimes \left( \langle x_1 | \langle x_2 | - \langle x_2 | \langle x_1 | \right) |\psi_{\text{f,0}}\rangle \otimes |1,0\rangle =
\]
\[
\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} \frac{1}{2^{\frac{1}{4}}} \left[ e^{iP(\langle x_1 \rangle \langle x_2 \rangle) / \hbar} H_1 \left( \frac{\mu \omega}{\hbar} (x_1 - x_2) \right) e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar}
- e^{iP(\langle x_2 \rangle \langle x_1 \rangle) / \hbar} H_1 \left( \frac{\mu \omega}{\hbar} (x_2 - x_1) \right) e^{-\mu \omega (x_2 - x_1)^2 / 2\hbar} \right]
= \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} \frac{1}{2^{\frac{1}{4}}} e^{iP(\langle x_1 \rangle \langle x_2 \rangle) / \hbar} e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar}
\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} \frac{1}{2^{\frac{1}{4}}} e^{iP(\langle x_2 \rangle \langle x_1 \rangle) / \hbar} e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar}
2 \cdot \frac{1}{\sqrt{2\pi \hbar}} \frac{(\mu \omega)}{\pi \hbar} (x_1 - x_2)
\]
since \( H_1(y)=2y \). For the probability density, the result is
\[
dP(x_1,x_2) = \frac{1}{8\pi \hbar} \sqrt{\frac{\mu \omega}{\pi \hbar}} e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar} 16 \frac{\mu \omega}{\hbar} (x_1 - x_2)^2 \, dx_1 \, dx_2
= \frac{1}{\pi \hbar} \sqrt{\frac{\mu \omega}{\pi \hbar}} 2 \frac{\mu \omega}{\pi \hbar} (x_1 - x_2)^2 \, e^{-\mu \omega (x_1 - x_2)^2 / 2\hbar} \, dx_1 \, dx_2
Problem 2)

To create properly anti-symmetrized wave functions, I would have to find three individual single-particle wave functions $|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle$ and antisymmetrize them using the Slater determinant. The result would obviously be zero unless all three wave functions are different in at least one aspect. If all three wave functions are eigenstates of the Hamiltonian of a single electron in the Coulomb field of a Lithium nucleus (3 x the Coulomb field of a hydrogen nucleus), then any product of them will be an eigenstate of the three-electron Hamiltonian (which, by assumption, is just the sum of the three single-particle hamiltonians) with the same eigenvalue, namely $E_1 + E_2 + E_3$. Therefore, the Slater determinant (which is a linear superpositions of such products) will also have that same eigenvalue. To find the lowest possible energy of the whole system, I have to find the lowest-energy single-electron eigenstates. Since $E = -\text{Ry} \frac{Z^2}{n^2}$, we need to use the lowest possible $n$'s. The very lowest is of course $n = 1$; this would in turn imply $\ell = 0$ and $m = 0$. Therefore, only two such wave functions are possible:

$$|\psi_1\rangle = |n = 1, \ell = 0, m = 0\rangle \otimes |\uparrow\rangle$$
$$|\psi_2\rangle = |n = 1, \ell = 0, m = 0\rangle \otimes |\downarrow\rangle$$

For the third one, we have to go to the next higher energy level, which by assumption is $n = 2$, $\ell = 0$ and $m = 0$. Again, two wave functions are possible (spin up and spin down), so we actually get two lowest energy eigenstates with the same eigenvalues (the degeneracy is 2). Both wave functions of course look very similar, so it is sufficient to write down just one:

$$|\psi_{1s,2s,1s}\rangle = |1,0,0\rangle \otimes |\uparrow\rangle$$
$$|\psi_{1s,2s,1s}\rangle = |1,0,0\rangle \otimes |\uparrow\rangle |2,0,0\rangle \otimes |\uparrow\rangle |1s \uparrow\rangle\rangle$$

Clearly, two of the three electrons are in a total spin $S=0$ $1s \times 1s$ state, while the remaining one is in an $2s$ spin up state. The total energy is

$$E_1 + E_2 + E_3 = -\text{Ry}Z^2 \left( \frac{1}{1^2} + \frac{1}{1^2} + \frac{1}{2^2} \right) = -13.6 \text{ eV} \frac{99}{4} = -275.4 \text{ eV}$$
**Problem 3**

Let’s consider each case in turn:

a) If both particles have spin $\frac{1}{2}$, they are Fermions and therefore must be in an overall antisymmetric state. Since their spatial state is already supposed to be antisymmetric, this means that their total spin state must be symmetric. As we have often discussed before, two spin-$1/2$ states coupling to a total spin-1 state yield a symmetric wave function, while spin-0 is antisymmetric. Therefore, the total spin must be 1.

b) If both particles have spin 1, they must be Bosons. This means that the total state must be symmetric under particle exchange. Given their antisymmetric spatial state, it follows that their total spin wave function must be antisymmetric as well, since two minus signs multiplied with each other yield a plus sign.

From the rules of addition of angular momentum, we can conclude that the only possible total spins of the combined state can be 0, 1 or 2. In total, we have 9 possible combinations ($|00\rangle$, $|11\rangle$, $|10\rangle$, $|1-1\rangle$, $|22\rangle$, $|21\rangle$, $|20\rangle$, $|2-1\rangle$, $|2-2\rangle$). We can express these in terms of products of one-particle states using Clebsch-Gordan coefficients:

$$
|00\rangle = \frac{1}{\sqrt{3}} |11\rangle |1-1\rangle - \frac{1}{\sqrt{3}} |10\rangle |10\rangle + \frac{1}{\sqrt{3}} |1-1\rangle |11\rangle
$$

Clearly, interchanging the first with the second particle simply interchanges the last with the first term (the middle one remains unchanged), and since both have the same sign, this spin state is symmetric and therefore impossible.

$$
|11\rangle = \frac{1}{\sqrt{2}} |11\rangle |10\rangle - \frac{1}{\sqrt{2}} |10\rangle |11\rangle; |10\rangle = \frac{1}{\sqrt{2}} |11\rangle |1-1\rangle - \frac{1}{\sqrt{2}} |1-1\rangle |11\rangle; |1-1\rangle = \frac{1}{\sqrt{2}} |10\rangle |1-1\rangle - \frac{1}{\sqrt{2}} |1-1\rangle |10\rangle
$$

Each one of these will change sign if we interchange the two single-particle spin states and are therefore antisymmetric. This means all states with total spin 1 are allowed.

$$
|22\rangle = |11\rangle |11\rangle; |21\rangle = \frac{1}{\sqrt{2}} |11\rangle |10\rangle + \frac{1}{\sqrt{2}} |10\rangle |11\rangle; |20\rangle = \frac{1}{\sqrt{6}} |11\rangle |1-1\rangle + \frac{2}{\sqrt{3}} |10\rangle |10\rangle + \frac{1}{\sqrt{6}} |1-1\rangle |11\rangle;
$$

$$
|2-1\rangle = \frac{1}{\sqrt{2}} |10\rangle |1-1\rangle + \frac{1}{\sqrt{2}} |1-1\rangle |10\rangle; |2-2\rangle = |1-1\rangle |1-1\rangle
$$

All of these once again are symmetric and therefore total spin 2 is not allowed.